

Attorney Docket: 030157-0304884
Client Reference:

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT APPLICATION of: ROBERT
VARRIN, ET AL.
Application No.: 10/762,500

Confirmation Number: 5230
Group Art Unit: 1751

Filed: January 23, 2004

Examiner: WEBB, Gregory E.

Title: SCALE CONDITIONING AGENTS AND TREATMENT METHOD

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DECLARATION UNDER 37 C.F.R. § 1.132

I, Robert D. Varrin, Jr., hereby declare as follows:

1. I have been an employee of Dominion Engineering, Inc. for fourteen years and have assumed a variety of different responsibilities over this time.
2. I am a co-inventor of the invention claimed in the above-captioned patent application.
3. U.S. Patent No. 4,632,705 ("Baum '705") states "[b]ulk concentration [of an organic acid such as EDTA] between 2-20% of previous recommendations." Baum '705, col. 5, line 9. Upon reading Baum '705, I understood this quoted passage to refer to a process wherein all accessible deposits (e.g., tube scale) had already been removed in a preceding cleaning process and reduced concentrations of EDTA would only be effective for removing residual crevice deposits if applied with periodic boiling to concentrate the cleaning agent within the crevices. I did not interpret this passage to refer to a process wherein bulk concentrations of less than 2% by weight on an absolute scale would be used for removal or structural modification of the bulk inventory of tube scale and deposits. If the Baum '705 process were applied to a steam generator that had not been previously cleaned to remove all accessible deposits from the free tube surfaces, it would be ineffectual for the cleaning of restricted areas such as crevices as Baum intended, because the EDTA would be rapidly consumed by the bulk deposits on the tubes.
4. Conventional chemical cleaning techniques typically result in corrosion of more than 0.001 inch per application in carbon and low allow steels, the primary structural materials used in heat exchangers and steam generators which may be cleaned using both conventional chemical cleaning techniques or the scale conditioning treatment method of one or more

embodiments of the above-captioned patent application. For example, in a typical corrosion allowance report prepared in support of an actual conventional chemical cleaning application, the corrosion allowance for carbon steel materials during a conventional chemical cleaning application was 0.0275 inch. The actual corrosion of carbon and low alloy steel components during this application ranged from 0.002 to 0.005 inch, which is typical for conventional chemical cleaning processes.

5. The chelant concentration of less than about 1% by weight in the aqueous cleaning solution, when combined with other appropriate chemical additives and under appropriate conditions according to one or more embodiments of the present invention, causes the chelant to not only react at the surface of the tube scale and deposits, but also penetrate below the surface to increase porosity within the deposits. If the deposits are present on a majority of heat transfer surfaces in the heat exchanger, the increased porosity advantageously improves heat transfer within the heat exchange system, which advantageously decreases fouling and increases steam pressure. The increased porosity occurs only with controlled, partial dissolution of the tube scale during the scale treatment method. Since conventional cleaning processes such as those described in U.S. Patent Number 5,601,657 ("Baum '657") and U.S. Patent Number 4,632,705 ("Baum '705") target complete removal of tube scale and deposits, the increased porosity and associated benefits are not possible. In one example, application of the scale treatment method according to an embodiment of the above-captioned patent application resulted in a 200% increase in relative tube scale porosity, from 10.3% to 31.1% absolute porosity [1]. This increase in porosity resulted in a 40 – 50 $\mu\text{hr}\cdot\text{ft}^2\cdot^\circ\text{F}/\text{Btu}$ decrease in fouling factor in the treated steam generators, which is equivalent to a 15 – 20 psi increase in steam pressure. As a consequence of improved thermal efficiency in the steam generators, plant electrical output was increased by roughly 0.5 – 2 MWe. The cost of such an increase in electrical output in the United States would be equivalent to about \$0.3 – 1 million, or perhaps more, per year.

6. I have been in the industry for 26 years, much of this time spent as a consultant and researcher in the area of chemical cleaning, and more specifically power plant heat exchanger and steam generator chemical cleaning, and have never seen any previous chelant-comprising cleaning process achieve similar results. In fact, it is not uncommon that complete removal of tube scale and deposits using higher concentration conventional chemical cleaning processes, which typically make use of 10 – 23% chelant, actually decreases heat transfer and

steam pressure. This phenomenon has been observed following a number of conventional chemical cleaning applications [2]. The industry has been surprised and impressed with the improved heat transfer and the increased porosity that cleaning methods using chelant concentrations of less than about 1% by weight have obtained according to one or more embodiments of the present invention, and leading chemical cleaning experts in the U.S., Canada, France, Japan, and Korea have repeatedly expressed their compliments on the success of the scale conditioning treatment method according to one or more embodiments of the present invention. License agreements have already been executed between our assignee and a major corporation in Japan, and negotiations are in progress in France, Canada, and Korea.

7. Intercalation agents such as those discussed in U.S. Patent No. 5,764,717 ("Rootham '717") bear no similarity in composition or functionality to chelant-based scale conditioning agents discussed in the above-captioned patent application. Specifically, the intercalation agents discussed in Rootham '717 were intended to insert and remove themselves from the crystalline structure of deposit species (primarily silicates), resulting in a "swelling" of chemical bonds and disruption of the overall deposit structure. However, negligible deposit material is removed by the intercalation agent as it would be by a chelant-based scale conditioning agent of one or more embodiments of the above-captioned patent application. Therefore, the intercalation agents described in Rootham '717 would not be expected, nor have they been observed, to increase the porosity of deposits in heat exchangers. This has been confirmed in numerous laboratory-scale evaluations conducted by Dominion Engineering, Inc. and in one full-scale field application. In fact, it has been determined that the intercalation agents discussed in Rootham '717 neither increase deposit porosity, nor disrupt the deposit structure, as intended by "swelling" of chemical bonds. As a result, intercalation agents have been abandoned by the industry as a means for removing or modifying the structure of scale and deposits in heat exchangers and steam generators. In contrast, the scale conditioning agents of one or more embodiments of the above-captioned patent application have been applied more than 10 times in the U.S. and Japan, and have only grown in popularity as additional industry experience is obtained. A full-scale demonstration of the scale conditioning treatment method according to an embodiment of the present invention will be performed in Korea for the first time in July 2007.

8. Oxidant cleaning solutions such as those described in U.S. Patent Number 4,578,162 ("McIntyre '162") are designed to remove only metallic copper from deposits. For comparison, the scale-conditioning agents according to one or more embodiments of the above-captioned patent application contain a reducing agent and target the removal of iron oxides (primarily magnetite) and other metallic oxides, which comprise a majority of the deposit matrix. Due to a combination of the relatively low concentration of copper present in deposits, the manner in which copper is distributed within the deposit matrix, and the selectivity of oxidant solutions for dissolving only metallic copper, exposure of deposits to oxidant solutions such as those described in McIntyre '162 would not be expected to result in a discernable increase in deposit porosity. Specifically, small and sparse metallic copper inclusions that are typically distributed uniformly throughout the deposit matrix, are selectively removed by the oxidant solutions, but the majority of the deposit matrix (>95%) is unaffected. This results in a negligible change to the overall deposit porosity. For comparison, the scale conditioning agents according to one or more embodiments of the above-captioned patent application achieve controlled, partially dissolution of magnetite and other deposit constituents which generally account for greater than 95% of the deposit structure by mass. As a result, scale conditioning treatment methods according to one or more embodiments of the above-captioned patent application result in increased deposit porosity, including the associated benefits discussed above. This has been confirmed in numerous laboratory-scale technical evaluations conducted by Dominion Engineering, Inc. and in numerous field applications (see Figure 1 and Figure 2).

9. Strict regulations prohibit used radioactive cleaning solutions from being released into the environment. Specifically, the limit for detection for gamma-emitting radionuclides such as Co-60, Co-58, or Cs-137 is on the order of $1 \times 10^{-8} \mu\text{Ci}$ per milliliter using standard analytical equipment. Any cleaning solutions in which radioactivity can be detected are classified as radioactive waste and must be processed accordingly. Experience has shown that if conventional chemical cleaning solvents, which typically contain 10-23% chelant, are used for complete deposit dissolution, this detection limit will be exceeded. However, scale conditioning agents described in one or more embodiments of the above-captioned patent application with chelant concentrations less about 1% by weight rarely result in generation of waste that is classified as radioactive. In seven out of eight times that cleaning methods according to one or more embodiments of the present invention have been used in heat

exchangers of nuclear steam generators, the resulting aqueous cleaning solution has been classified as non-radioactive. In the one scale conditioning agent application that resulted in the generation of radioactive waste, radioactivity was attributed to elevated leakage between the primary (radioactive) loop and secondary loop of the plant, not to the scale conditioning agent treatment method. Given that waste treatment costs range from \$10-30/gallon for used cleaning solutions classified as radioactive, and that waste volumes may be more than 100,000 gallons per application in a nuclear steam generator chemical cleaning, the savings associated with avoiding the generation of radioactive waste can be substantial. For comparison, disposal costs for non-radioactive liquid waste generated during a scale conditioning agent treatment as described in the above-captioned patent application, primarily transportation costs, typically range from \$0.5-1.0/gallon.

10. I hereby acknowledge that willful false statements and the like are punishable by fine or imprisonment, or both (18 USC Section 1001), and may jeopardize the validity of the present application or any patent issuing thereon. All statements made of my own knowledge are true, and all statements made on information and belief are believed to be true.



Robert D. Varrin, Jr.

July 2, 2007

Date

Pre-Test
Tube Scale

Expected Appearance
of Tube Scale Following
Exposure to Oxidant Solution

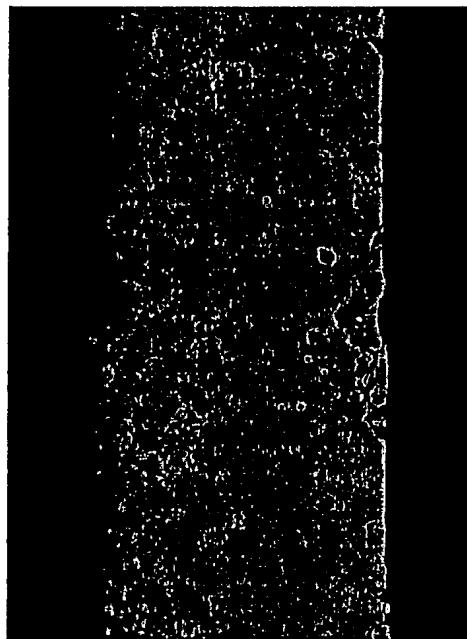
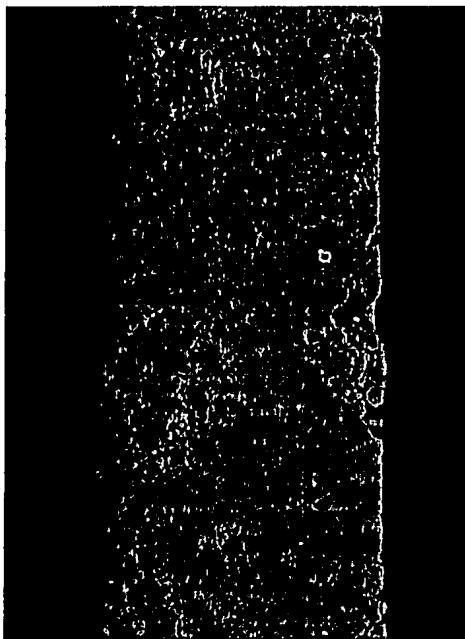
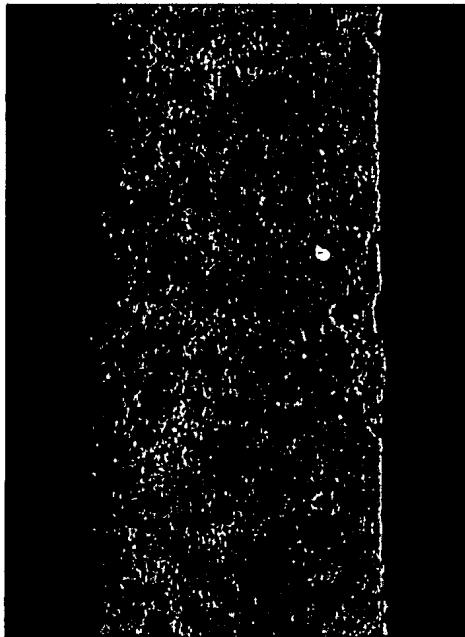


Figure 1 Microphotograph of Tube Scale Shown in Cross-Sectional View – Expected Changes in Scale Properties Resulting from Exposure to Oxidant Solutions (such as those described in McIntyre '162)

Note that oxidant solutions are expected to dissolve only copper inclusions, not iron oxides (primarily magnetite) or other primary deposit species. Since copper comprises only a small percentage of the overall deposit matrix by mass (typically on the order of 1%), negligible increase in porosity is expected as a result of exposure to oxidant solutions (such as those described in McIntyre '162).

Pre-Test
Tube Scale



Post-Test Tube Scale
Following Exposure to
Scale Conditioning Agent

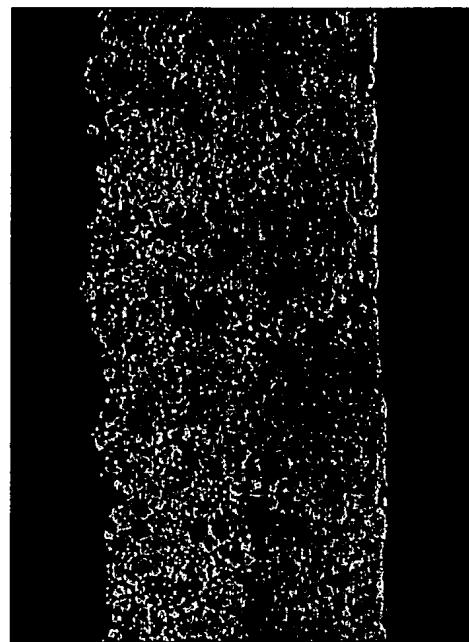


Figure 2 Microphotograph of Tube Scale Shown in Cross-Sectional View – Observed Increase in Deposit Porosity Resulting from Exposure to Scale Conditioning Agent of An Embodiment of the Above-Captioned Patent Application

Controlled, partial dissolution of iron oxide (magnetite) from the deposit surface and from within existing micropores results in increased deposit porosity (including creation of larger pores), which enhances boiling / heat transfer or facilitates more effective deposit removal by mechanical cleaning (depending on the specific objectives of the application).

References

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3. Scneidmiller, D and D. Sititeler, "Steam Generator Chemical Cleaning Process Development", Electric Power Research Institute (EPRI) NP-3009, April 1983.
4. Jevec, J. M. and W. S. Leedy, "Chemical Cleaning Solvent and Process Testing", Electric Power Research Institute (EPRI) NP-2976, April 1983.
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DECLARATION UNDER 37 C.F.R. § 1.132

I, Allen Baum, hereby declare as follows:

1. I am the inventor of U.S. Patent No. 4,632,705 ("Baum '705").
2. Baum '705 literally states "[b]ulk concentration [of an organic acid such as EDTA] between 2-20% of previous recommendations." However, the relative reduction in concentration depends on the concentration of the specific previous recommendations and reliance upon concentration of the agent by means of boiling action within the tube to tube support plate (TSP) crevices, where the agent is intended to act. I did not intend, and one of ordinary skill in the art would not have understood, this to mean bulk concentrations of less than 2% by weight on an absolute scale for removal or structural modification of the major inventory of tube scale and deposits. Further, I did not anticipate the benefit of using bulk concentrations of less than 2% in this manner.
3. The use of "[b]ulk concentration [of an organic acid such as EDTA] between 2-20% of previous recommendations" as stated in Baum '705 was intended only after all accessible deposits (e.g., tube scale) had already been removed in a preceding cleaning process and only a small percentage of deposits were remaining, primarily in TSP crevices. Lower bulk concentrations as stated in Baum '705 are feasible under these circumstances only because boiling action results in higher local concentrations of the active cleaning agent within TSP crevices, where deposits remain. Use of such low concentrations for bulk deposit removal or structural modification was neither anticipated nor intended in Baum '705. If the Baum '705 process were applied to a steam generator that had not been previously cleaned to remove all accessible deposits from the free tube surfaces, it would be ineffectual for the cleaning of

restricted areas such as crevices as I intended, because the EDTA would be rapidly consumed by the bulk deposits on the tubes.

4. I hereby acknowledge that willful false statements and the like are punishable by fine or imprisonment, or both (18 USC Section 1001), and may jeopardize the validity of the present application or any patent issuing thereon. All statements made of my own knowledge are true, and all statements made on information and belief are believed to be true.

Allen Baum

Allen Baum

July 3, 2007

Date